

MACHINE BUILDING AND MACHINE SCIENCE МАШИНОСТРОЕНИЕ И МАШИНОВЕДЕНИЕ



UDC 669.058.7(620.18+620.193)

Original article

<https://doi.org/10.23947/2687-1653-2023-23-2-140-154>

Aspects of Thermal Protection of Machine-Building and Power Equipment: Application of Oxidation-Resistant Combined Nickel-Based Coatings



Valeriy N. Varavka , Oleg V. Kudryakov , Vyacheslav I. Grishchenko

Don State Technical University, Rostov-on-Don, Russian Federation

✉ varavkavn@gmail.com

Abstract

Introduction. In the areas of power engineering where the thermal energy of superheated steam is used, an important aspect of providing the reliability and safety of equipment is the heat resistance of the materials employed. In the manufacture of induction superheaters, the optimal material for the steam pipe (coil) is copper. However, its ultimate resistance to oxidation does not exceed 400 °C, which significantly limits the efficiency of steam generators. Therefore, the objective of the work was to study the kinetics of oxidation of the combined galvanic coating of the Mo-Ni-Cr system applied to copper tubular samples and intended for thermal protection of steam generator coils.

Materials and Methods. A combined electroplating of the Mo-Ni-Cr system with a total thickness of 12–35 µm was formed on the experimental copper tubular samples. A Mo sublayer with a thickness of about 1.5 µm on the surface of the copper tube was formed to prevent the diffusion of Cu into the Ni coating. A 1.5 µm thick chromium layer on the coating surface acted as an indicator of the oxidation process. A comparative analysis of the oxidation processes of the copper surface and the combined coating of the Mo-Ni-Cr system on a copper substrate was carried out using the methods of optical and electron microscopy, energy dispersive analysis, and precision determination of the growth parameters of oxide films.

Results. The intervals of thermal stability of the copper substrate and nickel coating were experimentally determined. The obtained experimental dependences characterized the parabolic law of copper oxidation with the formation of a single-phase diffusion zone of CuO at temperatures above 350 °C, and nickel at temperatures above 750 °C, when the transition of NiO monoxide into oxide Ni₂O₃ began. The growth of oxide films according to quadratic laws provided a rapid increase in the thickness of the films, the accumulation of stresses in them, cracking, and chipping.

Discussion and Conclusion. It is shown that the Mo-Ni-Cr electroplating is resistant to heating during long-term operation up to temperatures of 750–800 °C. The functional roles of Mo and Cr in the coating architecture were described. The work focused on the applied aspect of using the coating under study to increase the thermal stability of the steam pipelines of industrial induction superheaters with low and medium power.

Keywords: superheaters, heat resistance, oxidation process, electroplating, microstructure, electron microscopy, gravimetric analysis

Acknowledgements: the authors would like to thank the editorial board of the journal and the reviewers for their attentive attitude to the article.

For citation. Varavka VN, Kudryakov OV, Grishchenko VI. Aspects of Thermal Protection of Machine-Building and Power Equipment: Application of Oxidation-Resistant Combined Nickel-Based Coatings. *Advanced Engineering Research (Rostov-on-Don)*. 2023;23(2):140–154. <https://doi.org/10.23947/2687-1653-2023-23-2-140-154>

Аспекты теплозащиты машиностроительного и энергетического оборудования: применение стойких к окислению комбинированных покрытий на основе никеля

В.Н. Варавка , О.В. Кудряков , В.И. Грищенко 

Донской государственный технический университет, г. Ростов-на-Дону, Российская Федерация

✉ varavkavn@gmail.com

Аннотация

Введение. В тех областях энергетического машиностроения, где используется тепловая энергия перегретого пара, важным аспектом обеспечения надежности и безопасности оборудования является теплостойкость используемых материалов. При изготовлении индукционных пароперегревателей оптимальным материалом для паропровода (змеевика) является медь. Однако её предельная стойкость к окислению не превышает 400 °С, что существенно ограничивает эффективность работы парогенераторов. Поэтому целью работы было исследование кинетики окисления комбинированного гальванического покрытия системы Mo-Ni-Cr, нанесенного на медные трубчатые образцы и предназначенного для теплозащиты змеевиков парогенераторов.

Материалы и методы. На опытных медных трубчатых образцах было сформировано комбинированное гальваническое покрытие системы Mo-Ni-Cr с общей толщиной 12–35 мкм. Подслой Mo толщиной около 1,5 мкм на поверхности медной трубки был сформирован для предотвращения диффузии Cu в Ni-покрытие. Слой хрома толщиной 1,5 мкм на поверхности покрытия выполнял роль индикатора процесса окисления. Сравнительный анализ процессов окисления поверхности меди и комбинированного покрытия системы Mo-Ni-Cr на медной подложке выполнен с использованием методик оптической и электронной микроскопии, энергодисперсионного анализа, а также прецизионного определения параметров роста оксидных пленок.

Результаты исследования. Экспериментально определены интервалы термической устойчивости медной подложки и никелевого покрытия. Полученные экспериментальные зависимости характеризуют параболический закон окисления меди с образованием однофазной диффузионной зоны CuO при температурах выше 350 °С и никеля при температурах выше 750 °С, когда начинается переход монооксида NiO и в оксид Ni₂O₃. Рост оксидных пленок по квадратичным законам приводит к быстрому увеличению толщины пленок, накоплению в них напряжений, растрескиванию и скалыванию.

Обсуждение и заключение. Показано, что гальваническое покрытие Mo-Ni-Cr устойчиво к нагреву при длительной эксплуатации вплоть до температур 750–800 °С. Описаны функциональные роли Mo и Cr в архитектуре покрытия. Работа акцентирована на прикладном аспекте использования исследуемого покрытия для повышения термической устойчивости змеевика-паропровода промышленных индукционных пароперегревателей малой и средней мощности.

Ключевые слова: парогенераторы, теплостойкость, окислительный процесс, гальванические покрытия, микроструктура, электронная микроскопия, гравиметрический анализ

Благодарности: авторы выражают благодарность редакции журнала и рецензентам за внимательное отношение к статье.

Для цитирования. Варавка В.Н., Кудряков О.В., Грищенко В.И. Аспекты теплозащиты машиностроительного и энергетического оборудования: применение стойких к окислению комбинированных покрытий на основе никеля. *Advanced Engineering Research (Rostov-on-Don)*. 2023;23(2):140–154. <https://doi.org/10.23947/2687-1653-2023-23-2-140-154>

Introduction. Electrochemical deposition of metals is widespread in industry, being the basis of electroplating. One of the features of the development of this branch of science is usually attributed to the fact that its development took place “almost exclusively empirically” [1], starting primarily from the needs of various industries. Despite the fact that at present, the theoretical foundations of electrochemistry have been worked out quite deeply [2–6], the applied aspect is

still of priority importance here and determines most of the scientific tasks being solved, mainly related to the special conditions for the use of electroplating coatings. Under such particular conditions, superheaters are operated, for example, whose performance is associated with a significant change in the composition and temperature of steam along the length of the steam coil [7]. Depending on the power of the steam generator, the temperature of the coil along its length can vary from 150 to 650 °C, and for super-critical steam parameters in high-capacity modern steam turbines — even higher [8–10]. This work studies the possibility of using electroplating coatings to protect the steam pipe of an induction superheater from oxidation at high temperatures. On the totality of physical and technological properties (electrical conductivity, thermal conductivity, ability to plastic deformation, machinability by cutting, etc.), copper is currently an indispensable structural material for the manufacture of coils for household and low-power industrial steam generators. This is the reason for the interest in heat-protective coatings. However, the oxidizing ability of copper is also high, and its oxidation resistance does not exceed 400 °C. Based on the operating conditions of the superheaters under consideration, this circumstance offers a challenge of using coatings whose oxidation resistance level is above the thermal barrier of 600 °C.

Materials and Methods. Taking into account the complex configuration of the coil, the presence of a large length of curved surfaces and its considerable overall dimensions, electrochemical deposition was chosen as the most technologically advanced method of applying a heat-protective coating.

To select the composition of such a coating, accurate data on its operating modes were required. For this purpose, a thermal imaging analysis of the thermal operating conditions of an experimental induction three-coil six-turn steam generator with a capacity of 10 kW was carried out (Fig. 1) [11]. The steam pipe was made of profiled copper tube $\varnothing 25 \times 1.5$ mm of technical copper M2 grade according to GOST 617–2006.

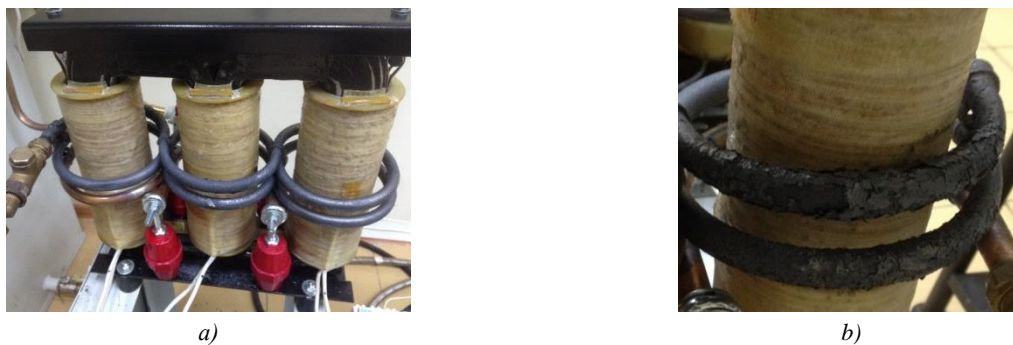


Fig. 1. Experimental induction superheater with copper steam pipe: *a* — general view; *b* — the most heavily oxidized sections of the steam pipe (coil) at the steam outlet

Quantitative thermal analysis of the operating conditions of the steam pipeline, including forced operating modes, was performed using a no-contact thermal imager of Fluke Ti401 PRO model (manufactured by Fluke Corp., USA) [12] with the main technical characteristics:

- infrared spectral range: from 7.5 to 14 μm (long-wavelength);
- thermal sensitivity: ≤ 0.075 °C at an object temperature of 30 °C (75 mK);
- error: ± 2 °C (at low temperatures) or 2%;
- degree of protection: according to GOST 14254-96 (IEC 60529): IP54.

The heat capacity of water vapor ($c_p = 33.6$ J/(mol·K) under normal conditions) is approximately twice lower than the heat capacity of water ($c_p = 75.3$ J/(mol·K)), which changes significantly the conditions of heat removal in the coil and contributes to the intensification of oxidation of the surface of the steam pipe; therefore, substantial heterogeneity of the degree of oxidation is observed along its length (Fig. 1 *b*). The thermal analysis results (Fig. 2) showed that the maximum heating temperatures were fixed at the output half-turn of the coil (Fig. 1 *b*). The range of their values was 530–540 °C with an absolute maximum of 541.38 °C. The average temperature values of most superheated (oxidized) half-turns were at the level of 420–460 °C.

Taking into account the results obtained, in further studies on heat-resistant coatings to protect against oxidation of the coil surface, it is needed to focus on the maximum temperature load of 600 °C. In this regard, it is reasonable to use

nickel-based coatings. Ni forms the basis of most modern heat-resistant superalloys used in thermal power engineering [13–15], and the technology of electroplating Ni is quite well developed [15–18].

When applying experimental electroplating coatings to samples of copper tubes of technical copper M2, standard deposition modes and compositions of electrolytes containing Ni and Cr recommended by GOST 9.305 and 9.306 were used. During the operation of the steam generator, the coating is practically not subjected to mechanical action; therefore, it should not demonstrate outstanding mechanical properties during performance. At the same time, when applied to a curved convex surface, internal tensile stresses are formed in the coating. As the number of working heat shifts increases, their level grows. In this regard, the thickness of the investigated coating on the steam line should not be too large. It was taken as the average of the recommended in the literature ranges of values for nickel electroplating coatings performing protective and decorative functions, and was an approximate level of 20 μm .

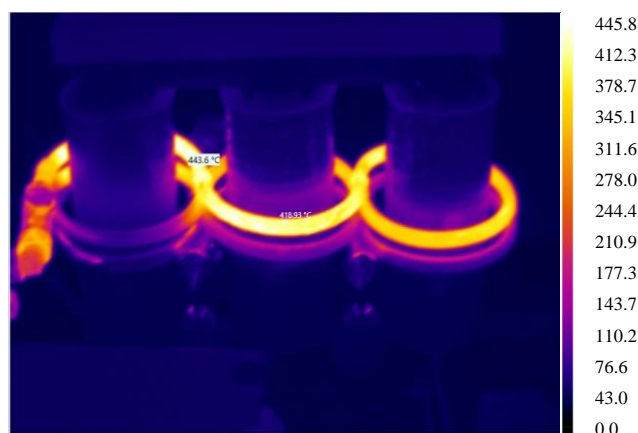


Fig. 2. IR image of a general view of the thermal fields of a working superheater (the window of the Fluke Connect program, the location of the coil is similar to Fig. 1 a, all values are in degrees Celsius)

To study the microstructure of coatings and the topography of their surface, dual beam (electron/ion) scanning electron microscope ZEISS CrossBeam 340 (SEM) was used, which provides using a focused ion beam (FIB) to etch and perform cross-sections (sections of a given configuration) of samples directly in the vacuum chamber of the microscope with high positioning accuracy. The elemental composition of the studied surfaces was monitored using energy dispersive X-ray detector (EDAX) of X-Max 50N (Oxford Instruments) model, built into an electron microscope.

The study of the oxidation kinetics of coatings was carried out through measuring the mass index of high-temperature gas corrosion (weight gain of the sample as a result of heating and oxidation). To determine the degree of oxidation of copper samples, both coated and uncoated, all samples were weighed before and after experiments at different stages of interaction. Gravimetric studies were carried out on analytical scales of “VLR-20” brand with a weighing accuracy of 10^{-5} g.

Results and Discussion

1. Qualitative analysis of oxidation kinetics. Properties of the chemical interaction of nickel and oxygen are manifested in the fact that Ni forms two modifications of monoxide: α -NiO with a hexagonal lattice (below 252 °C) and β -NiO with a face-centered cubic lattice. The transition occurs under continuous heating in the range of 250–300 °C. It was experimentally established that when heated to 630 °C, a diffusion process ran through a thin film of NiO monoxide, above 640 °C, a chemical process of NiO formation was established, which, when heated above temperatures of 800 °C, could cause the formation of Ni_2O_3 oxide [19].

The applied aspect of using a heat-resistant nickel coating on a copper substrate was complicated by two circumstances: the unlimited solubility of the Cu-Ni system components (Fig. 3) and the possibility of the Kirkendall interaction effect [21, 22] at the “Ni-coating — Cu-substrate” boundary. These phenomena reduced the resistance of the coating to oxidation due to the dissolution of copper in the coating.

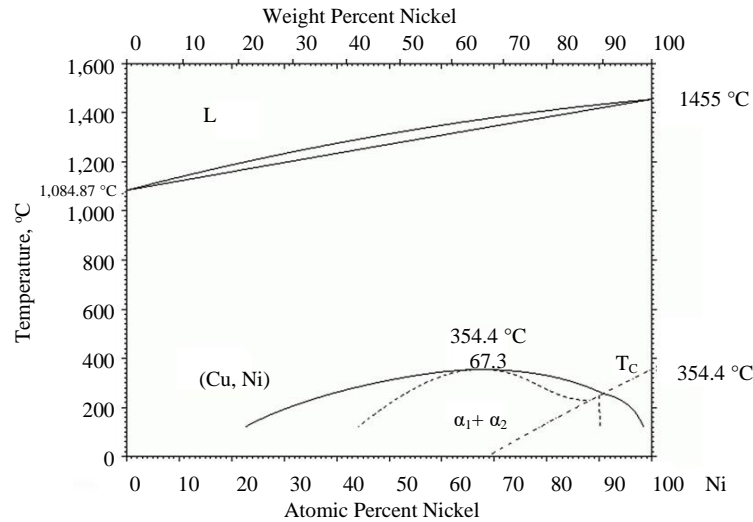


Fig. 3. Diagram of the phase states of the copper-nickel system [20]

To exclude the negative impact of these circumstances on the oxidation resistance of the coating, a combined electroplating of the Mo-Ni-Cr system was formed on experimental copper tubular samples (рис. 4). Mo sublayer with a thickness of about 1.5 μm on the surface of the copper tube (Fig. 4 *b*) was formed to prevent the diffusion of Cu into the Ni coating under long-term operation of the steam pipe due to the practically insoluble system of Cu-Mo components and the limited solubility of Ni-Mo [20]. A layer of chromium 1.5 μm thick on the coating surface (Fig. 4 *b*) served as an indicator of the oxidation process (for more information, see below). The total thickness of the coating on the experimental samples with coatings was 12–35 μm . The elemental distribution in the cross-section of the initial Mo-Ni-Cr coating (before the experiment with sample heating) is shown in Fig. 5.

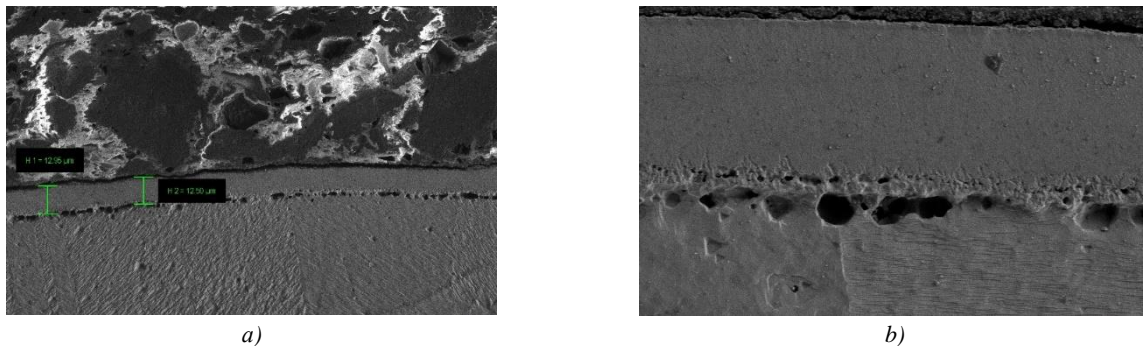
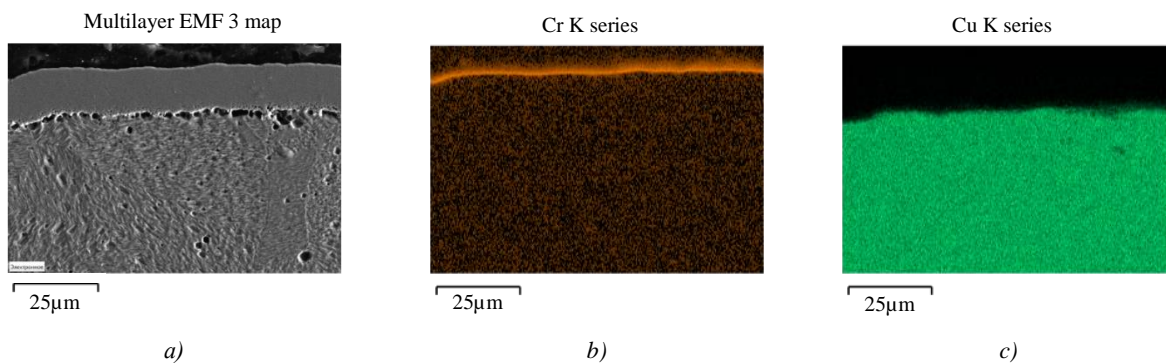


Fig. 4. Initial MoNiC coating in cross section, SEM: *a* — coating with thickness markers; *b* — homogeneous microstructure of the coating and hydrogen porosity at the boundary with the substrate



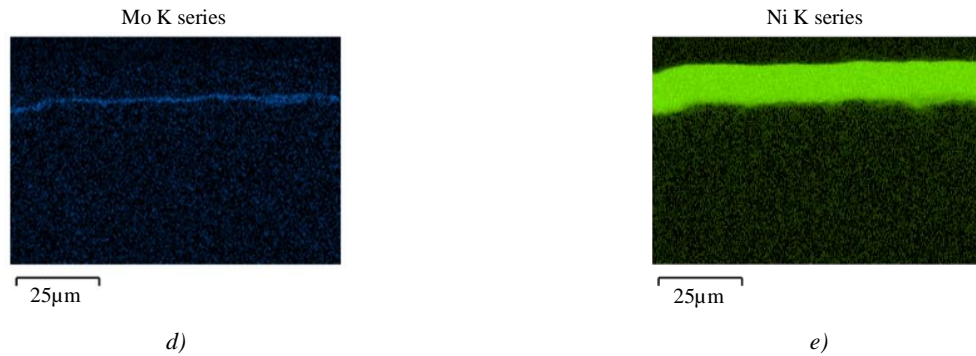


Fig. 5. Color maps of the distribution of chemical elements by the depth of Mo-Ni-Cr coating, EDAX: *a* — general view of the coating in cross-section (SEM); *b–e* — distribution of elements in general view image: Cr (*b*), Cu (*c*), Mo (*d*), Ni (*e*)

For the experimental study of the oxidation kinetics under conditions as close as possible to the operating conditions of the steam pipe, the samples for the study were made of copper tubes with the corresponding wall thickness and diameter (Fig. 6).

After plating with the technology that included heat treatment elements [11], the coating acquired a greenish hue characteristic of nickel monoxide NiO. When operating the steam pipe, the coating was applied only to the outer (convex) surface of the samples. However, in order to correctly determine the weight gain of the coating on the experimental samples, the coating was applied on both sides.

Simultaneous heating of pure copper samples and coated samples was carried out at a fixed temperature in the range of 350–1000 °C in SNOL 6.7/1300 (2.4 kW) furnace in air. Exposure at a given temperature was 30 minutes. For the statistical picture of the experiment, heating at each set temperature was carried out for 5–7 samples with their separate loading into the furnace. The selective results of the experiment are visualized in Figure 7.

From the experimental data obtained, it follows that under the conditions of the conducted heating, copper is relatively thermally-resistant to a temperature of 300–350 °C. At these temperatures, a dense thin oxide film of brown color is formed on the copper surface, regardless of its curvature (Fig. 7).



Fig. 6. Samples for the study of oxidation kinetics; external surfaces of reference samples of pure copper (right) and copper coated with Mo-Ni-Cr (left), prepared for experiments



Fig. 7. Comparison of the outer surface of the samples after heating to the specified temperatures: on the left — coated samples, on the right — pure copper samples

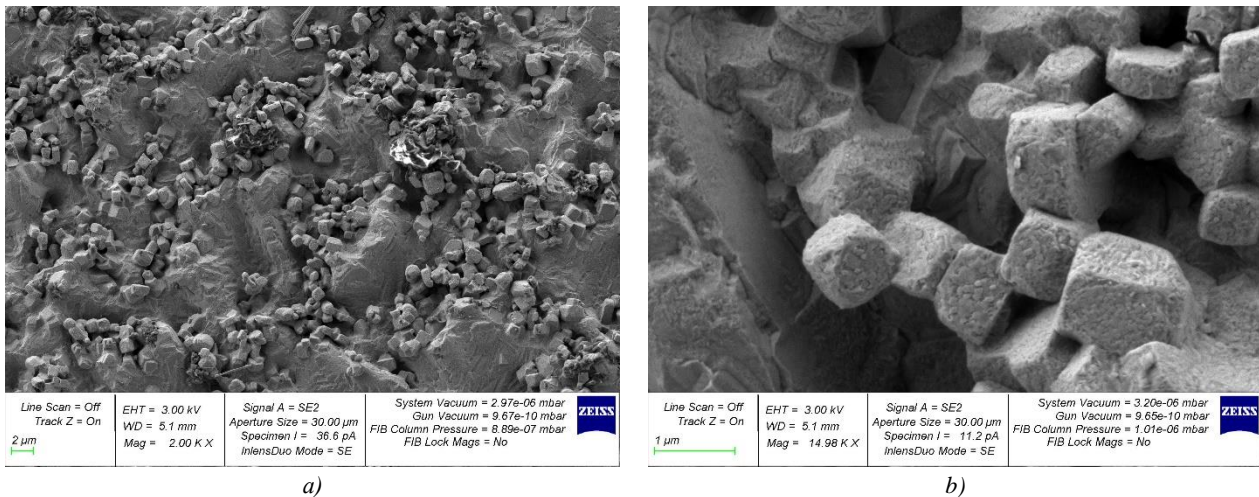


Fig. 8. Copper surface of the sample oxidized at a temperature of 650 °C, SEM: *a* — location of CuO crystals on the copper surface; *b* — morphology of CuO crystallites

According to the literature data [23, 24], it appears to be two-layered: a thin sublayer of Cu_2O is located on the surface of the sample, and a layer of CuO is located outside. Due to the small thickness of the latter, the internal stresses in the film are small. It has good adhesion to the substrate, low roughness, it does not loosen, and does not chip off the surface. As the heating temperature increases, the growth of the outer oxide layer CuO accelerates. Already at a temperature of 450 °C, it becomes very loose and crumbles from the surface (Fig. 1 *b*). At the same time, a Cu_2O sublayer of a characteristic reddish hue is found under it (Fig. 7). During further heating, peeling and shedding of the CuO oxide layer progresses — it practically does not stay on the surface up to temperatures of 650–700 °C. This, apparently, is due to the nature of crystallization of copper monoxide: its crystallites have a strict cut close to cubic (Fig. 8 *b*), weak conjugation with each other, and, most importantly, high heterogeneity of the nucleation sites (Fig. 8 *a*). Starting from the heating temperatures of ≈ 750 °C, the copper oxide film is compacted, the strength of its adhesion to the surface increases. On the concave surface of the samples, due to compressive configuration stresses, the CuO film is strong enough or can peel off completely from the entire surface of the sample without crumbling. At temperatures of 800–900 °C, the CuO oxide film behaves similarly on the outer (convex) surface of the samples.

The surface of samples coated with Mo-Ni-Cr practically does not change up to a heating temperature of 750 °C. Upon further heating above 800 °C, the coating is first covered with a film of Cr_2O_3 oxide having a characteristic bright green color (Fig. 7). Then, at heating temperatures above 900 °C, the deeper layers of the coating are oxidized. Amphoteric chromium oxide Cr_2O_3 (Fig. 9 *b*) is fundamentally different in its morphology and crystallization character from CuO copper monoxide (Fig. 8). Cr_2O_3 oxide crystals have a characteristic polyhedron shape with a predominance of prismatic crystallites. Due to the large dispersion of crystallites in size, they, unlike copper monoxide, form a layer on the surface with a high packing density of crystallites.

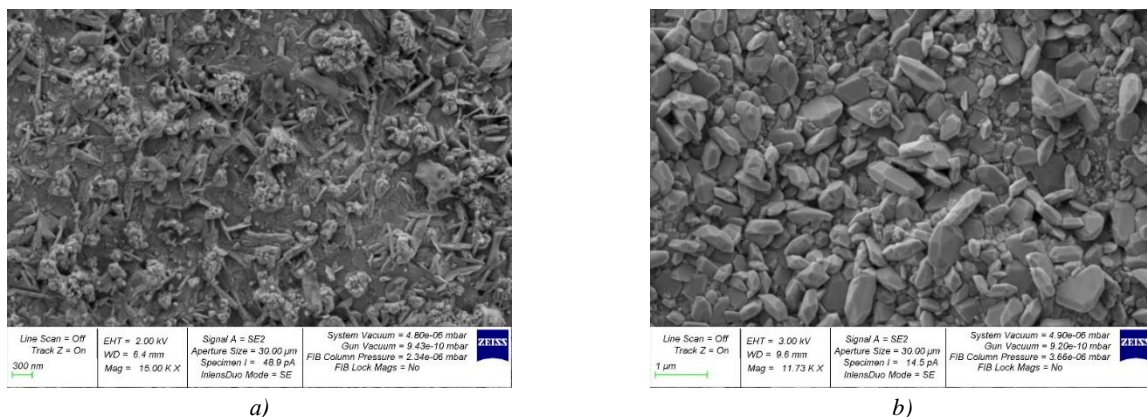


Fig. 9. Surface of samples coated with Mo-Ni-Cr, SEM:

a — after heating to a temperature of 650 °C; *b* — after heating to a temperature of 850 °C

If, prior to the oxidation of the chromium layer (below 800 °C), the coating surface has a very weak crystallinity character (Fig. 9 a), then the appearance of Cr₂O₃ oxide gives the surface a well-known polycrystalline appearance (Fig. 9 b). In general, the nickel coating does not change its composition and structure by cross-section up to a temperature of 850 °C (Fig. 10). The chemical composition of the coating surface at this temperature indicates the initial degree of oxidation of the chromium layer. The presence of a thin layer of chromium oxide on the surface is confirmed by the data of energy dispersion analysis (EDAX) both by the depth of the coating and by the surface. Figure 11 shows that oxygen is concentrated in a much narrower surface layer (~1 µm) than the chromium layer (~3 µm), which characterizes the initial stage of oxidation.

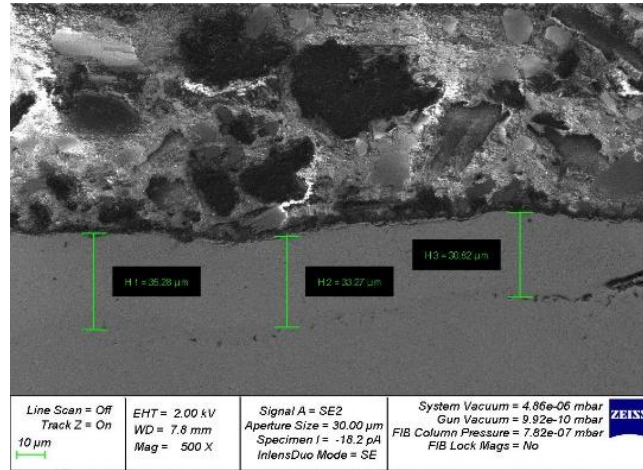
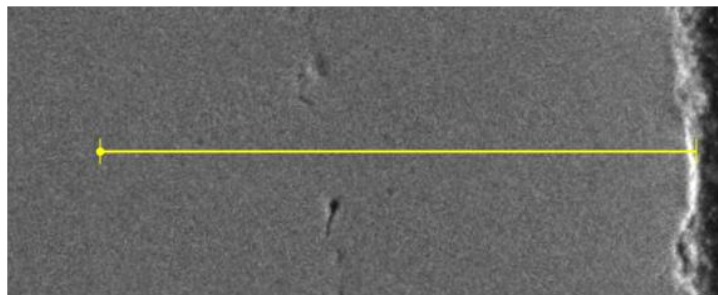
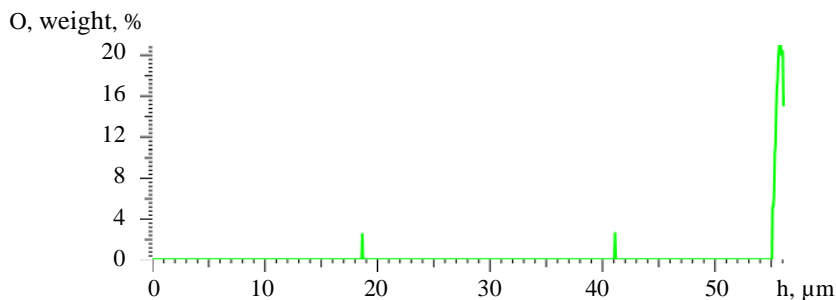


Fig. 10. Thickness and structure of Mo-Ni-Cr coating in cross section after heating up to 850 °C, SEM

To reduce the volume of the article, the EDAX data is not provided in full. Its results show that the amount of oxygen on the surface increases from 30 to 50 at. % due to a similar decrease in chromium concentration, which indicates the oxidation of chromium (since the concentration of Ni does not change when heated from 650 °C to 850 °C, and the presence of Ni in the detection results is caused by the penetration of X-ray radiation through a thin layer of chromium into the nickel base of the coating during EDAX analysis). The composition of the oxides corresponds to the compound Cr₂O₃.



a)



b)

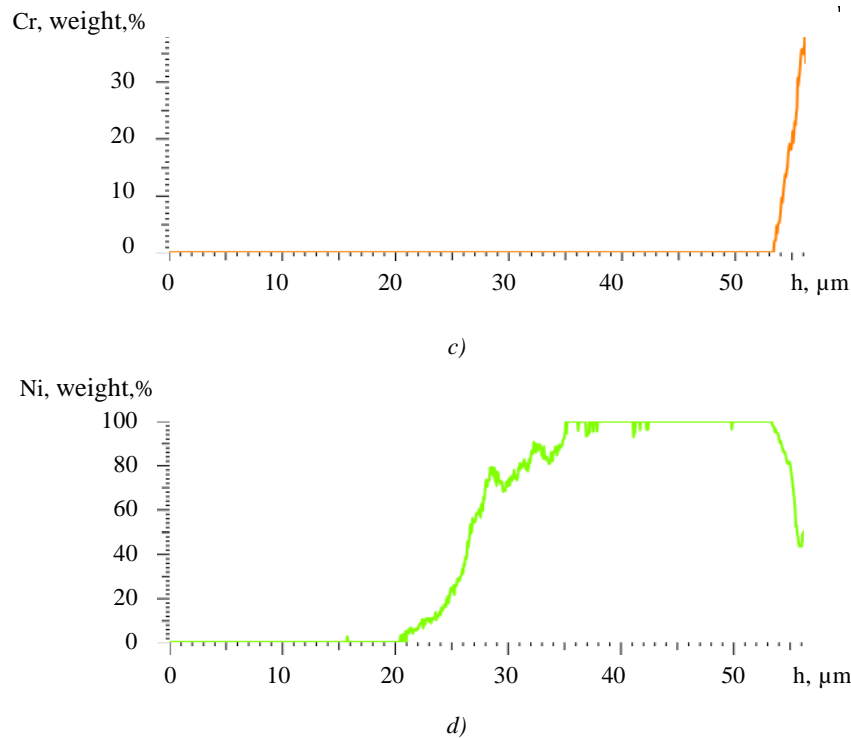


Fig. 11. Distribution of the main chemical elements in Mo-Ni-Cr coating by depth h after heating to 850 °C, EDAX:
a — coating in cross section, the scanning direction (SEM) is shown; *b–d* — content of elements in the scanning direction;
b — oxygen; *c* — chromium; *d* — nickel

All stages of the oxidation process of the coating are shown in Figure 12. At temperatures above 800 °C, the surface of the coating starts to oxidize, as indicated by a change in its color — the coating acquires the Kensington Green color.

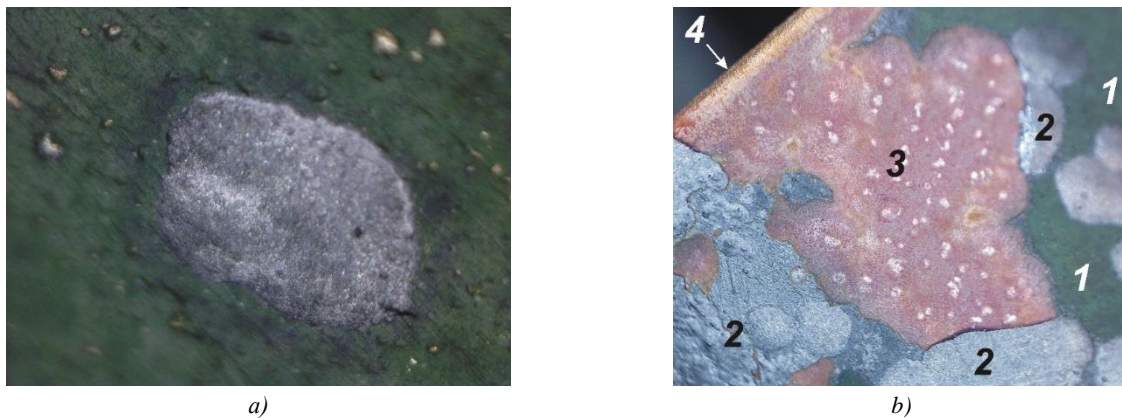


Fig. 12. Successive stages of oxidation of nickel coating, optical microscopy, $\times 100$: *a* — initial stage: germination of nickel oxide (dark-gray precipitates) on the surface of chromium oxide (green field) at 850 °C; *b* — final stage: collective phase pattern in the area of coating chip at 1,000 °C, where:
 1 — chromium oxide Cr_2O_3 ; 2 — nickel oxide Ni_2O_3 ; 3 — copper surface (coating chip); 4 — sample edge

This color corresponds to chromium oxide Cr_2O_3 . Already at a temperature of 850 °C, rare single formations of Ni_2O_3 nickel oxide can be found on the surface of the coating (Fig. 12 *a*, gray color), which, under further heating, gradually increase their area occupied on the surface. As they grow, which mainly spreads tangentially to the surface, under the impact of internal stresses, the Ni_2O_3 oxide film cracks and then chips off, exposing the surface of the substrate — pure copper of a reddish hue (Fig. 12 *b*).

Thus, the basic result of this part of the research should be considered experimentally established temperature ranges of permissible use of materials for the manufacture of steam pipe of steam generator. Thus, a copper steam pipe without

coatings is operable up to a temperature of 300 °C and can only be used to generate wet (not overheated) steam. Starting from a temperature of ~400 °C and up to ~700 °C, the CuO oxide film formed is very loose and easily crumbles from the copper surface. At higher temperatures, the film becomes denser, thicker, and its adhesion to the copper substrate increases. However, it is still prone to chipping during heat exchange. Its presence on the surface of the steam pipe significantly slows down the heat removal, and the chemical reactions of high-temperature gas corrosion that continue during heating, work in the direction of reducing the thickness of the pipe. Due to the heterogeneity of the ongoing processes, the operation of the steam pipe under these conditions becomes unpredictable from the point of view of emergency situations. The use of a combined electroplating of the Mo-Ni-Cr system increases the efficiency of the steam pipe to a temperature of 750–800 °C. When the temperature reaches 850 °C, the coating starts to oxidize along with copper. At 950 °C and above, the oxidized coating is prone to chipping, and its operation is subject to the same risks as the copper pipe. A distinctive feature of the investigated coating is self-testing: if the heating temperature exceeds 800 °C during operation, the surface layer of chromium turns the coating bright green and signals the danger of overheating. The indicator layer of galvanic chrome after oxidation can be easily restored, and the operation of the steam pipe then continues.

Quantitative analysis of oxidation kinetics

As part of the performed studies, a quantitative analysis of the kinetics of oxidation of pure copper samples and Mo-Ni-Cr coated samples was carried out. The specific mass gain $M = \Delta m / S$, observed during the heating process, was used as a measured parameter, where Δm — increase in the mass of the sample, g; S — area of the oxidized surface of the sample, cm². According to the qualitative analysis method described above, the experimental data of M values were obtained during the heating of tubular samples made of pure copper and coated samples. They are presented in Tables 1 and 2.

The Tables show the spread intervals of the data obtained for fixed values of heating temperatures (Table 1) or the holding time in the furnace (Table 2), as well as the average value of M from each interval.

Statistical processing of the data shown in Tables 1 and 2, performed using the MathCAD application software package, which included interpolation procedures, allowed us to obtain kinetic dependences shown in Figures 13 and 14. The rectilinear graphs of the obtained dependences, shown in Figure 13 *b* in Arrhenius coordinates ($-\ln M - 1,000/T$), characterized the parabolic law of oxidation of copper at temperatures above 350 °C and nickel — at temperatures above 750 °C [19, 25–27].

Table 1

Experimental data on the specific mass gain of samples under furnace heating in air for 30 min

No. of experiment	Furnace temperature, °C	Specific weight gain M , 10 ⁻⁵ g/cm ²	
		Uncoated copper tube	Ni-coated copper tube *
1	350	1.35 ± 0.31	—
2	450	6.23 ± 1.37	—
3	550	24.73 ± 3.60	—
4	650	58.51 ± 9.02	1.52 ± 0.24
5	750	138.88 ± 17.85	4.25 ± 0.58
6	850	241.03 ± 25.25	13.12 ± 1.08
7	1,000	564.70 ± 49.76	35.71 ± 2.78

* minimum weight gain equal to 10⁻⁵ g, measured on the analytical scales, was taken for the criterion of the absence of oxidation (dash in the Table)

Table 2

Experimental data on specific mass gain of samples at different exposure time in the air of the furnace

No. of experiment	Holding time in the furnace, min	Specific weight gain M , 10^{-5} g/cm ²	
		Uncoated copper tube at 600 °C	Ni-coated copper tube at 800 °C
1	5	13.68 ± 2.02	3.03 ± 0.41
2	15	29.43 ± 4.15	5.93 ± 0.54
3	30	35.76 ± 4.84	7.11 ± 0.67

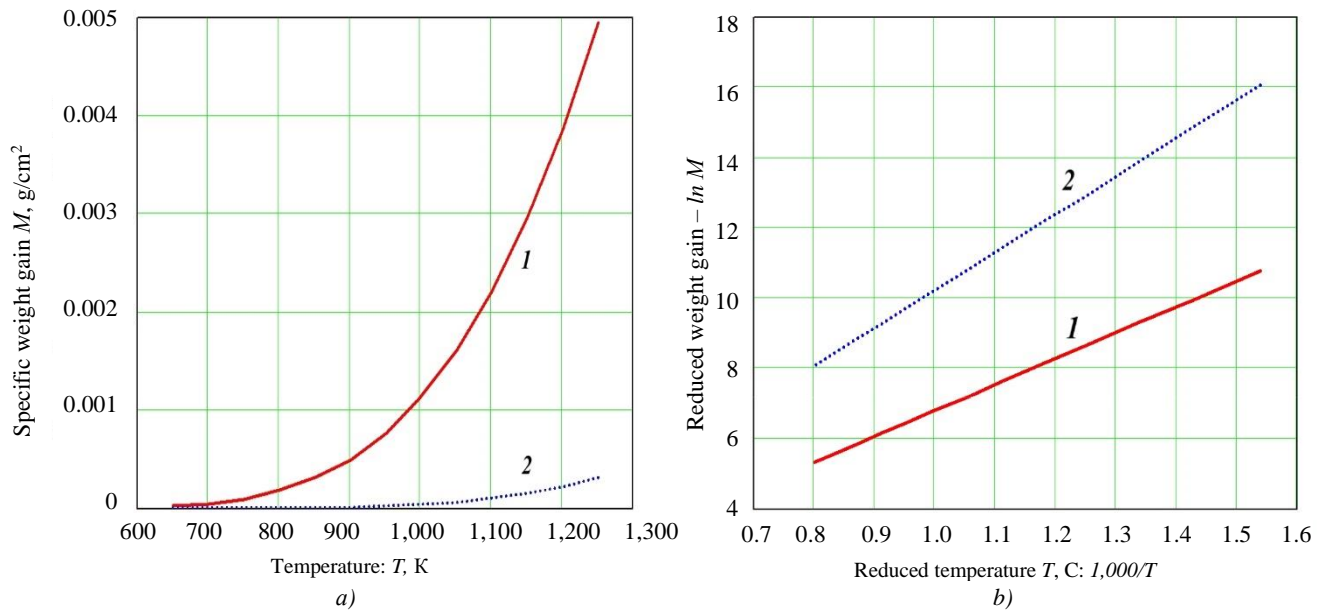


Fig. 13. Temperature dependences of mass gain M of pure copper samples (1) and samples coated with Mo-Ni-Cr (2):
a — in absolute units; b — in relative coordinate system

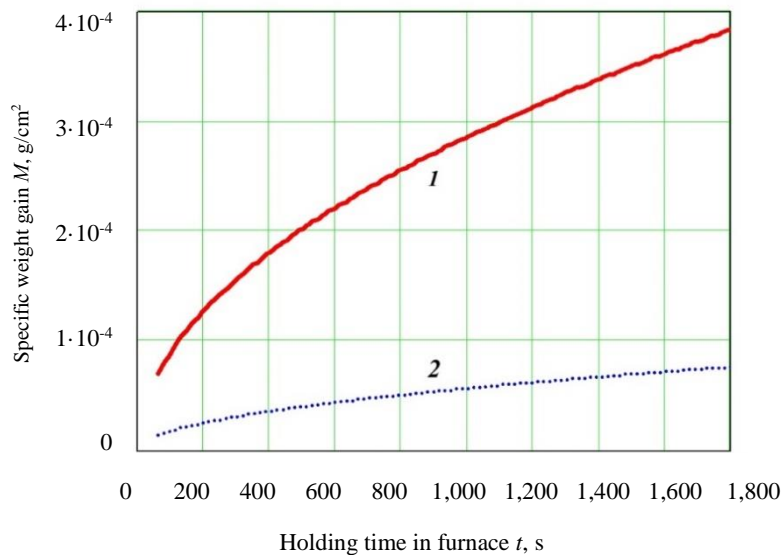


Fig. 14. Kinetics of time variation of mass gain M of pure copper samples at 600 °C (1) and samples coated with Mo-Ni-Cr at 800 °C (2)

The growth of oxide films according to quadratic laws occurs with the formation of single-phase diffused zones, in this case consisting of CuO and NiO oxides, respectively. It causes a rapid increase in the thickness of the films, the accumulation of stresses in them, cracking and chipping. An additional contribution to the acceleration of this process is made by the curved outer surface of the copper tube [28, 29].

Conclusions

1. The performed set of studies has shown that the combined electroplating of the Mo-Ni-Cr system is a sufficiently effective protection of the copper steam pipe from oxidation. The coating is able to provide a long-term operation of the steam generator up to heating temperatures of 750–800 °C.

2. Long-term heat resistance of the coating is provided by an internal Ni layer with a recommended thickness of 20–30 µm. The study of the oxidation kinetics of the coating, performed by optical and electron microscopy, energy dispersion analysis, as well as using precision methods for determining the growth parameters of oxide films, has shown that the nickel coating is indifferent to heating up to temperatures of 600–650 °C. In the temperature range 700–900 °C, the oxidation of the coating occurs with the formation of NiO monoxide according to the parabolic law. At higher temperatures, oxidation progresses due to the formation of Ni₂O₃ oxide film, which quickly causes its growth, cracking and chipping.

3. The combined architecture of the investigated nickel coating includes two thin layers of Mo and Cr. The Mo sublayer with a thickness of about 1.5 µm is located on the surface of the copper tube (substrate). Its function is to prevent the mutual diffusion of Ni and Cu at the coating – substrate interface during long-term operation of the steam generator, since the dissolution of copper reduces the heat resistance of nickel and disrupts the performance of the coating. The outer layer of chromium with a thickness of 2–3 µm serves as an indicator of the degree of oxidation of the coating. The first sign of excessive oxidation of the coating is the appearance of a bright green hue on the surface of the coating, which is associated with the formation of chromium oxide Cr₂O₃ at temperatures ≥800 °C. The overheating indicator — a layer of chromium — is easily updated and contributes to the prolongation of the life cycle of the steam generator.

References

1. Knauschner A. *Oberflächenveredeln und Plattieren von Metallen*. Leipzig: VEB Deutscher Verlag Grundstoffindustrie; 1982. 416 p.
2. Stock JT, Orna MV (eds.). *Electrochemistry, Past and Present*. Washington, DC: American Chemical Society; 1989. 606 p.
3. Gamburg YuD. *Gal'vanicheskie pokrytiya*. Moscow: Tekhnosfera; 2006. 216 p. (In Russ.)
https://www.elec.ru/files/2019/09/23/Galvanicheskie_pokrytia_Spravochnik_po_primeneniyu.PDF (accessed: 10.02.2023).
4. Andreev YuYa. *Ehlektrokimiya metallov i splavov*. Moscow: MISiS; 2011. 256 p. (In Russ.)
5. Ujjal Kumat Sur (ed.). *Recent Trend in Electrochemical Science and Technology*. London: IntechOpen; 2012. 318 p.
<https://doi.org/10.5772/1891>
6. Djokic SS (ed.). *Modern Aspects of Electrochemistry*. New York, NY: Springer; 2014. P. 1–84.
7. Song Liu, Yaping Wei, Shiqiang Chen, et al. Development and Application of an Ultrahigh-Temperature Steam Generator. *Advances in Materials Science and Engineering*. 2020;2020:4243170. <https://doi.org/10.1155/2020/4243170>
8. Weitzel PS, Tanzosh JM, Boring B, et al. *Advanced Ultra-Supercritical Power Plant (700 to 760 °C) Design for Indian Coal*. In: Proc. POWER-GEN Asia Conference and Exhibition. Bangkok, 2012. P. 281–291.
9. Wang Chongbin, Xu Xueyuan, Zhu Yufeng, et al. Research on the Heating Surface Material Properties for 700 °C USC Boiler. In book: *Energy Materials*. Cham: Springer; 2014. P. 151–159. URL: https://link.springer.com/chapter/10.1007/978-3-319-48765-6_16 (accessed: 10.02.2023).
10. Booras GS, Powers JM, Riley C, et al. *Engineering and Economic Analysis of an Advanced Ultra-Supercritical Pulverized Coal Power Plant with and without Post-Combustion Carbon Capture*. Palo Alto, CA: Electric Power Research Institute; 2015. 111 p.

11. Shipilov VM, et al. *Ehlektricheskii paroperegrevatel'*. RF Patent, No. 2736270. 2020. 11 p. (In Russ.)
12. *Teplovizor Fluke Ti401 PRO*. URL: <https://fluke-russia.ru/catalog/teplovizor-fluke-ti401-pro> (In Russ.) (accessed: 02.02.2023).
13. Sims ChN, et al. (eds.). *Superalloys II: High-Temperature Materials for Aerospace and Industrial Power*. New York, NY: John Wiley & Sons; 1987. 640 p.
14. Reed RC. *The Superalloys. Fundamentals and Applications*. Cambridge: Cambridge University Press; 2006. 372 p. <https://doi.org/10.1017/CBO9780511541285>
15. Toshio Narita, et al. Advanced Coatings on High Temperature Applications. *Materials Science Forum*. 2006;522–523:1–14. <https://doi.org/10.4028/www.scientific.net/MSF.522-523.1>
16. Yuebo Zhou, Peng X, Wang F. Oxidation of a Novel Electrodeposited Ni–Al Nanocomposite Film at 1050 °C. *Scripta Materialia*. 2004;50(12):1429–1433. <https://doi.org/10.1016/j.scriptamat.2004.03.014>
17. Karimzadeh A, Aliofkhaezrai M, Walsh FC. A Review of Electrodeposited Ni–Co Alloy and Composite Coatings: Microstructure, Properties and Applications. *Surface Coatings Technology*. 2019;372:463–498. <https://doi.org/10.1016/j.surfcoat.2019.04.079>
18. Morteza Alizadeh, Abbas Cheshmpish. Electrodeposition of Ni–Mo/Al₂O₃ Nano-Composite Coatings at Various Deposition Current Densities. *Applied Surface Science*. 2019;466:433–440. <https://doi.org/10.1016/j.apsusc.2018.10.073>
19. Ryabukhin AG, Novoselova EG, Samarin II. Okislenie nikelya na vozdukhe s obrazovaniem tonkikh plenok. *Bulletin of the South Ural State University. Series "Metallurgy"*. 2005;10:34–40. (In Russ.)
20. *Fazovye diagrammy dvoynykh system*. URL: <https://himikatus.ru/art/phase-diagr1/diagrams.php> (In Russ.) (accessed: 10.02.2023).
21. Bhadeshia HKDH. *Kirkendall Effect*. University of Cambridge. URL: <http://www.phase-trans.msm.cam.ac.uk/kirkendall.html> (accessed: 10.02.2023).
22. Hideo Nakajima. The Discovery and Acceptance of the Kirkendall Effect. *Journal of The Minerals, Metals & Materials Society (JOM)*. 1997;49(6):15–19. <https://doi.org/10.1007%2Fb02914706>
23. Yao Zhi Hu, Rahul Sharangpani, Sing-Pin Tay. Kinetic Investigation of Copper Film Oxidation by Spectroscopic Ellipsometry and Reflectometry. *Journal of Vacuum Science & Technology A*. 2000;18(5):2527–2532. <https://doi.org/10.1116/1.1287156>
24. Avetisyan AG, Chatilyan HA, Kharatyan SL. Kineticheskie osobennosti nachal'nykh stadii vysokotemperaturnogo okisleniya medi. *Chemical Journal of Armenia*. 2013;66(3):407–415. URL: <https://www.researchgate.net/publication/271459151> (In Russ.) (accessed: 10.02.2023).
25. Haugsrud R. On the High-Temperature Oxidation of Nickel. *Corrosion Science*. 2003;45(1):211–235. [https://doi.org/10.1016/S0010-938X\(02\)00085-9](https://doi.org/10.1016/S0010-938X(02)00085-9)
26. Mrowec S, Grzesik Z. Oxidation of Nickel and Transport Properties of Nickel Oxide. *Journal of Physics and Chemistry of Solids*. 2004;65(10):1651–1657. <https://doi.org/10.1016/j.jpcs.2004.03.011>
27. Avetisyan A, Chatilyan NA, Kharatyan SL. Kineticheskie osobennosti nachal'nykh stadii vysokotemperaturnogo okisleniya nikelya. *Chemical Journal of Armenia*. 2014;67(1):27–35. URL: <https://www.researchgate.net/publication/271458661> (accessed: 10.02.2023).
28. Karmhag R, Tesfamichael T, Wäckelgard E, et al. Oxidation Kinetics of Nickel Particles: Comparison Between Free Particles and Particles in an Oxide Matrix. *Solar Energy*. 2000;68(4):329–333. [https://doi.org/10.1016/S0038-092X\(00\)00025-6](https://doi.org/10.1016/S0038-092X(00)00025-6)
29. Lei Zhou, Ashish Rai, Nicholas Piekiet, et al. Ion-Mobility Spectrometry of Nickel Nanoparticle Oxidation Kinetics: Application to Energetic Materials. *Journal of Physical Chemistry C*. 2008;112(42):16209–16218. <https://doi.org/10.1021/jp711235a>

Received 13.03.2023

Revised 29.03.2023

Accepted 05.04.2023

About the Authors:

Valeriy N. Varavka, Dr.Sci. (Eng.), Professor of the Materials Science and Technology of Metals Department, Head of “Materials” Research and Educational Center, Don State Technical University (1, Gagarin sq., Rostov-on-Don, 344003, RF) [ResearcherID](#), [ScopusID](#), [ORCID](#), [AuthorID](#), varavkavn@gmail.com

Oleg V. Kudryakov, Dr.Sci. (Eng.), Professor of the Materials Science and Technology of Metals Department, Don State Technical University (1, Gagarin sq., Rostov-on-Don, 344003, RF) [ResearcherID](#), [ScopusID](#), [ORCID](#), [AuthorID](#), kudryakov@mail.ru

Vyacheslav I. Grishchenko, Cand.Sci. (Eng.), Associate Professor, Head of the Hydraulics, Hydropneumoaوماتics and Heat Management Department, Head of “Spektr” Technical Engineer Center, Don State Technical University (1, Gagarin sq., Rostov-on-Don, 344003, RF), , [ResearcherID](#), [ScopusID](#), [ORCID](#), [AuthorID](#), vig84@yandex.ru

Claimed contributorship:

VN Varavka: academic advising; basic concept formulation; research objectives and tasks; discussion of the results; text preparation; formulation of conclusions.

OV Kudryakov: planning and organization of experiments; conducting metal-physical studies; analysis of the results obtained; correction of the conclusions.

VI Grishchenko: preparation of the experimental base, samples and equipment; technical management of the experimental research process; computational analysis; discussion of the results.

Conflict of interest statement: the authors do not have any conflict of interest.

All authors have read and approved the final manuscript.

Поступила в редакцию 13.03.2023

Поступила после рецензирования 29.03.2023

Принята к публикации 05.04.2023

Об авторах:

Валерий Николаевич Варавка, доктор технических наук, профессор кафедры материаловедения и технологии металлов, директор НОЦ «Материалы» Донского государственного технического университета (344003, РФ, г. Ростов-на-Дону, пл. Гагарина, 1) [ResearcherID](#), [ScopusID](#), [ORCID](#), [AuthorID](#), varavkavn@gmail.com

Олег Вячеславович Кудряков, доктор технических наук, профессор кафедры материаловедения и технологии металлов Донского государственного технического университета (344003, РФ, г. Ростов-на-Дону, пл. Гагарина, 1) [ResearcherID](#), [ScopusID](#), [ORCID](#), [AuthorID](#), kudryakov@mail.ru

Вячеслав Игоревич Грищенко, кандидат технических наук, доцент, заведующий кафедрой гидравлики, гидропневмоавтоматики и тепловых процессов, руководитель ИТЦ «Спектр», Донского государственного технического университета (344003, РФ, г. Ростов-на-Дону, пл. Гагарина, 1) [ResearcherID](#), [ScopusID](#), [ORCID](#), [AuthorID](#), vig84@yandex.ru

Заявленный вклад соавторов:

В.Н. Варава — научное руководство, формирование основной концепции, цели и задачи исследования, обсуждение результатов, подготовка текста, формирование выводов.

О.В. Кудряков — планирование и организация экспериментов, проведение металлофизических исследований, анализ полученных результатов, корректировка выводов.

В.И. Грищенко — подготовка экспериментальной базы, образцов и оборудования, техническое руководство процессом экспериментальных исследований, выполнение расчетов, обсуждение результатов.

Конфликт интересов: авторы заявляют об отсутствии конфликта интересов.

Все авторы прочитали и одобрили окончательный вариант рукописи.